

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

Date of mailing (day/month/year) 17 November 2000 (17.11.00)	To: Commissioner US Department of Commerce United States Patent and Trademark Office, PCT 2011 South Clark Place Room CP2/5C24 Arlington, VA 22202 ETATS-UNIS D'AMERIQUE in its capacity as elected Office
International application No. PCT/GB00/01251	Applicant's or agent's file reference RTM3
International filing date (day/month/year) 31 March 2000 (31.03.00)	Priority date (day/month/year) 31 March 1999 (31.03.99)
Applicant TASKER, Peter, Anthony et al	

1. The designated Office is hereby notified of its election made:

in the demand filed with the International Preliminary Examining Authority on:

26 October 2000 (26.10.00)

in a notice effecting later election filed with the International Bureau on:

2. The election was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Zakaria EL KHODARY Telephone No.: (41-22) 338.83.38
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PATENT COOPERATION TREATY
PCT
INTERNATIONAL PRELIMINARY EXAMINATION REPORT

REC'D	19 JUN 2001
WIPO	PCT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference RTM	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/GB00/01251	International filing date (<i>day/month/year</i>) 31/03/2000	Priority date (<i>day/month/year</i>) 31/03/1999
International Patent Classification (IPC) or national classification and IPC C02F1/68		
Applicant THE UNIVERSITY COURT OF THE UNIVERSITY OF EDINBURG		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets, including this cover sheet.

This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 6 sheets.

3. This report contains indications relating to the following items:

- I Basis of the report
- II Priority
- III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV Lack of unity of invention
- V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI Certain documents cited
- VII Certain defects in the international application
- VIII Certain observations on the international application

Date of submission of the demand 26/10/2000	Date of completion of this report 15.06.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Grigoraki, E Telephone No. +49 89 2399 8353



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/01251

I. Basis of the report

1. With regard to the elements of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):
Description, pages:

2-6,9-22	as originally filed		
1,7,8	as received on	24/05/2001 with letter of	21/05/2001

Claims, No.:

1-11	as received on	24/05/2001 with letter of	21/05/2001
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2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:
- the drawings, sheets:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB00/01251

5. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N) Yes: Claims 2-11
 No: Claims 1

Inventive step (IS) Yes: Claims 2-11
 No: Claims 1

Industrial applicability (IA) Yes: Claims 1-11
 No: Claims

2. Citations and explanations
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB00/01251

Conclusion V:

(1)

As acknowledged in the description, on page 3, l. 1-20 of the description, bifunctional ligands for simultaneous binding of cations and anions are already known. Present claim 1 now defining in a broader manner than originally a method of extracting both the cations and anions of a metal salt from an aqueous medium by contacting it with such bifunctional ligand is not considered novel or is at least not inventive in view of the cited prior art on page 3 of the application.

Claim 1 does not therefore fulfil the requirements of article 33(2) or (3) PCT.

(2)

The above cited prior art in the application apparently does not suggest the effective multiple use of such ligands after binding cations and anions from aqueous media and selectively stripping and recovering them from the thus obtained complex.

DE-A-3607982 (D1) cited in search report apparently does not disclose the use of bifunctional ligands and the formation of a complex with all three of them. D1 moreover uses onium salts the cations of which form with anions of the aqueous phase non soluble salts in the organic phase and the anions thereof form with the cations of the aqueous phase soluble salts which are precipitated.

The use of such bifunctional ligands with the purpose of recovering the cations and anions from an aqueous medium and upon stripping recovering the ligand for reuse as defined in present claim 2 can be regarded as a novel and inventive concept.

Claim 2 in combination with claim 1 and dependent claims thereon 3-11 would therefore fulfil the requirements of article 33(2) and (3) PCT.

EXTRACTION OF METAL SALTSField of the invention

5 This invention relates to the extraction of metal salts from aqueous solutions. More specifically it relates to methods for extracting metal cations and their associated anions which avoid returning any ionic species to the solution, thus leaving the acidity of the solution unchanged and purifying it by deionisation. Methods according to the invention are of use particularly (though not exclusively) in waste remediation and in the recovery of metals from primary sources.

Background

15 Two main methods are currently used for the extraction of metallic ions from solution. Both involve the use of an extractant reagent: in the first method this is mixed with the solution from which the metal ions are to be removed ("solvent extraction"), and in the second it is immobilised on a solid support.

20 Current solvent extraction technology is based on a system in which an acidic extractant is used to remove a metal cation from an aqueous feed stream. The metal n^+ cation is replaced by n protons and the anion is left in the solution. The overall effect on the feed stream is to replace a metal salt MX with a mineral acid H_nX and this leads to an increase in the acidity of the aqueous feed stream.

25 This type of reaction is widely used for the extraction of copper from oxidic ores, the acid introduced into the stream reacting with insoluble metal oxides to give soluble metal salts. Indeed, this reaction scheme is particularly suited to the extraction of metals from metal oxides since the overall reaction has a perfect
30 mass balance equation:

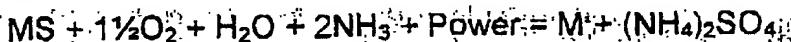


phenolic protons are then displaced and protonate the nitrogen atoms of the tertiary amine groups, producing a positively charged binding site for the anion. The precise binding mechanism for the Type I ligands has yet to be elucidated.

Use of either class of ligand is effective to remove both the cations and anions of a metal salt from the feed stream. When decontamination of the feed stream is the sole aim, removal of the metal salt may be regarded as an end in itself. In most cases, however, it is desired to extract the cations as elemental metal, and indeed this is the primary aim of ore extraction methods. A major advantage of the method of the invention is that the anion may also be retrieved; for instance the anion (such as sulphate) may be precipitated as an ammonium salt, which may then be used as fertiliser. As a result, this ligand is regenerated in unbound form, and may be recycled for future use.

The method of cation and anion precipitation depends on the class of ligand. For Type I ligands, contact with an aqueous ammoniacal solution liberates an ammoniacal solution of the metal salt from which the metal can be electrolysed. The electrolysis step produces metal and acid. Continual addition of ammonia to the system is required to neutralise the acid produced, and a by product of the reaction is an ammonium salt. For Type II ligands, the metal cation may also be recovered by contacting with strong acid. The metal cation M^{n+} in the hydrocarbon solution is replaced by n protons generating the 'acid' form of the reagent LH_nX . This allows electrolysis of the metal from an acidic medium. The resulting solution is then contacted with ammonia solution, regenerating the reagent L and producing an ammonium salt as a by product.

In each case the overall reaction is the same. The overall mass balance for this system is:



30

In a waste remediation application, for example removal of metal salts

from acid drainage streams, the overall mass balance is:



5 The Type 1 ligands are known in the literature, though not for the purpose of
 removing metal salts from aqueous solutions as in the present invention; their
 synthesis will therefore not be described herein. To illustrate the efficacy of
 ligands of this type in removing metal salts from aqueous solution, a 0.1M
 10 solution in toluene of Type I ligand ($R_1 = R_2 = R_3 = -\text{CH}_2\text{CH}_2-$; $R_4=R_5=\text{C}_9\text{H}_{19}$) was
 contacted with an 0.1M aqueous solution of nickel sulfate. A light blue toluene
 solution was formed, analysis of which showed that approximately 80% of both
 Ni^{2+} and SO_4^{2-} ions had been transferred to the organic phase.

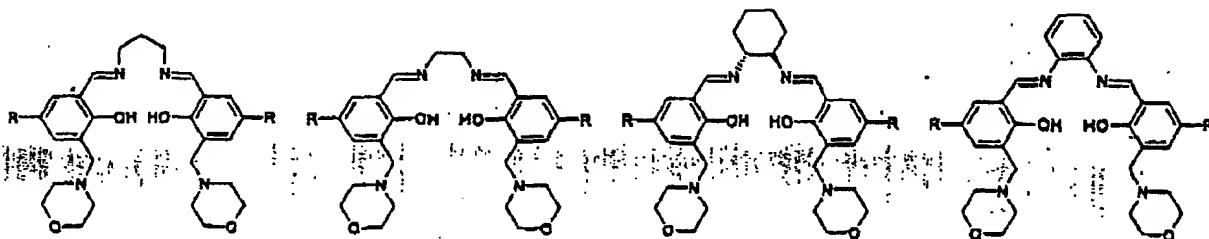
Detailed description

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The invention is described hereinafter in more detail with reference to the
 synthesis and activity of various ligands of the Type II formula. The following is a
 representative sample of various different Type II ligands.

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Me 4

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t-Bu 8

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Nonyl 12

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CLAIMS

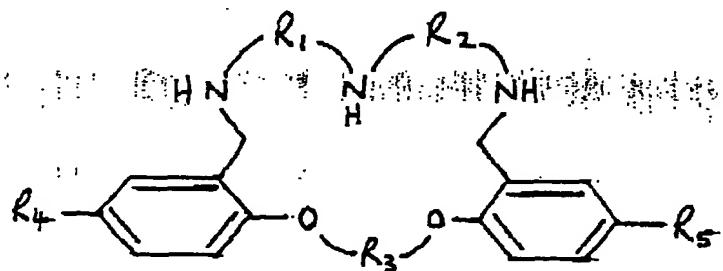
1. A method of extracting both the cation(s) and anion(s) of a metal
 5 salt from an aqueous medium, the method comprising the step of contacting the aqueous medium with a bifunctional ligand capable of binding both said cation(s) and said anion(s) so as to form a complex comprising said ligand and said cation(s) and anion(s).

10 2. A method according to claim 1, further comprising the steps of: selectively stripping and recovering said cations(s) and said anions(s) from said complex; and recovering said ligand, free of said cations(s) and anion(s), for future use.

15 3. A method according to claim 1 or claim 2, wherein the ligand has a greater affinity for a water-immiscible extraction medium than it does for said aqueous medium, the method involving the steps of: adding a said water-immiscible extraction medium to said aqueous medium, whereby said ligand with said cation(s) and said anion(s) bound thereto is partitioned preferentially in
 20 a water-immiscible phase; and separating said water-immiscible phase with said ligand-bound cation(s) and anion(s) therein from said aqueous medium.

25 4. A method according to claim 1 or claim 2, wherein the ligand is immobilised on or within a solid support.

5. A method according to any preceding claim, wherein the ligand is of the following formula:



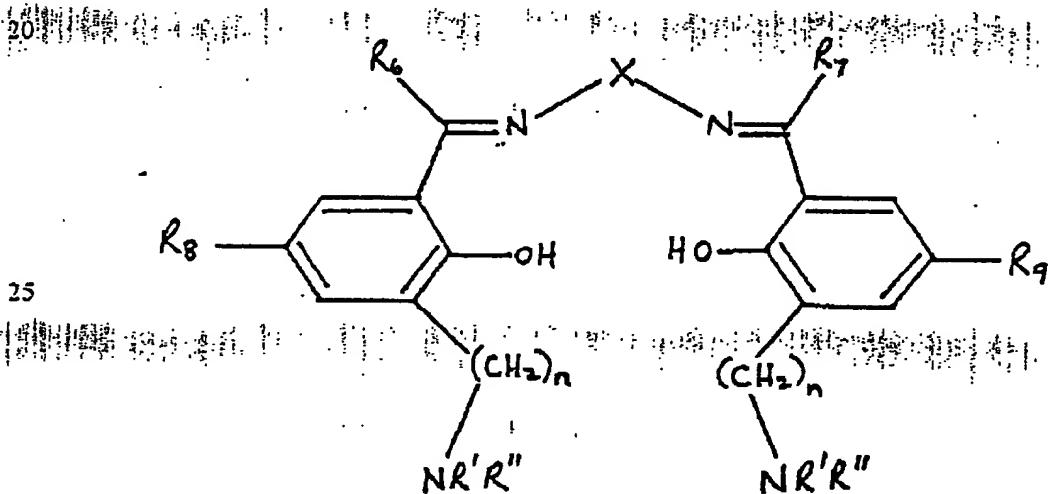
where R_1 , R_2 and R_3 are independently substituted C_2 to C_4 linkages; and

5 R_4 and R_5 are independently H or an optionally halogenated aliphatic or aromatic hydrocarbon group.

6. A method according to claim 5, comprising the further steps of: contacting the ligand-bound salt with an aqueous ammoniacal solution to 10 produce an aqueous ammoniacal solution of the metal salt; and electrolysing said solution to produce elemental metal and an ammonium salt.

7. A method according to any of claims 1 to 4, wherein the ligand has 15 a cation binding site comprising at least one coordinating acid group and an anion binding site comprising at least one protonatable base.

8. A method according to claim 5, wherein the ligand has the following formula:



where

X represents a C₂ to C₄ linkage, in which the carbon atoms may be substituted or unsubstituted and may optionally form part of a ring structure;

n = 2, 3 or 4;

R₆, R₇, R₈ and R₉ are each, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon; and

R'R" are tertiary amine groups, the R' and R" groups optionally forming a heterocyclic ring.

15 9. A method according to claim 7 or claim 8, comprising the further steps of: contacting the ligand-bound salt with a strong acid to protonate the ligand and release the metal cation(s); and electrolysing the resulting solution to product elemental metal.

20 10. A method according to claim 9, comprising the further step of contacting the ligand-bound anion(s) with an ammoniacal solution, to neutralise said solution and produce an ammonium salt.

25 11. A method according to any of claims 8 to 10, wherein NR'R" is a morpholine or piperidine ring.

The demand must be filed directly with the competent International Preliminary Examining Authority or, if two or more Authorities are competent, with the one chosen by the applicant. The full name or two-letter code of that Authority may be indicated by the applicant on the line below:

IPEA/ EP

PCT

CHAPTER II

DEMAND

under Article 31 of the Patent Cooperation Treaty:

The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated).

For International Preliminary Examining Authority use only

Identification of IPEA

Date of receipt of DEMAND

Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION		Applicant's or agent's file reference RTM
International application No. PCT/GB00/01251	International filing date (day/month/year) 31st March 2000 (31.03.00)	(Earliest) Priority date (day/month/year) 31st March 1999 (31.03.99)
Title of invention EXTRACTION OF METAL SALTS FROM AQUEOUS SOLUTIONS		
Box No. II APPLICANT(S)		
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) The University Court of The University of Edinburgh, Old College, South Bridge, Edinburgh EH8 9YL, United Kingdom	Telephone No.:	
	Facsimile No.:	
	Teleprinter No.:	
State (that is, country) of nationality: United Kingdom	State (that is, country) of residence: United Kingdom	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) TASKER, Peter Anthony 25 Braid Avenue, Edinburgh United Kingdom		
State (that is, country) of nationality: United Kingdom	State (that is, country) of residence: United Kingdom	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) WHITE, David James 3 Roachill Close, Altrincham, Cheshire, United Kingdom.		
State (that is, country) of nationality: United Kingdom	State (that is, country) of residence: United Kingdom	
<input type="checkbox"/> Further applicants are indicated on a continuation sheet.		

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The following person is agent common representative

and has been appointed earlier and represents the applicant(s) also for international preliminary examination.

is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked.

is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.

Name and address: (*Family name followed by given name: for a legal entity: full official designation.
The address must include postal code and name of country.*)

Telephone No.:

0207 405 0356

Facsimile No.:

0207 831 9628

Teleprinter No.:

MANATON, Ross Timothy
J.Y. & G.W. Johnson
Kingsbourne House,
229-231 High Holborn,
London WC1V 7DP,
United Kingdom

Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Box No. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION**Statement concerning amendments:***

1. The applicant wishes the international preliminary examination to start on the basis of:

the international application as originally filed

the description as originally filed

as amended under Article 34

the claims as originally filed

as amended under Article 19 (together with any accompanying statement)

as amended under Article 34

the drawings as originally filed

as amended under Article 34

2. The applicant wishes any amendment to the claims under Article 19 to be considered as reversed.

3. The applicant wishes the start of the international preliminary examination to be postponed until the expiration of 20 months from the priority date unless the International Preliminary Examining Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69.1(d)). (*This check-box may be marked only where the time limit under Article 19 has not yet expired.*)

- * Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.

Language for the purposes of international preliminary examination: English

which is the language in which the international application was filed.

which is the language of a translation furnished for the purposes of international search.

which is the language of publication of the international application.

which is the language of the translation (to be) furnished for the purposes of international preliminary examination.

Box No. V ELECTION OF STATES

The applicant hereby elects all eligible States (*that is, all States which have been designated and which are bound by Chapter II of the PCT*)

excluding the following States which the applicant wishes not to elect:

Box No. VI CHECK LIST

The demand is accompanied by the following elements, in the language referred to in Box No. IV, for the purposes of international preliminary examination:

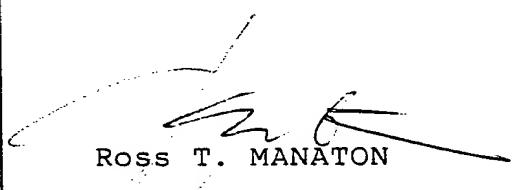
			For International Preliminary Examining Authority use only	
			received	not received
1. translation of international application	:	sheets	<input type="checkbox"/>	<input type="checkbox"/>
2. amendments under Article 34	:	sheets	<input type="checkbox"/>	<input type="checkbox"/>
3. copy (or, where required, translation) of amendments under Article 19	:	sheets	<input type="checkbox"/>	<input type="checkbox"/>
4. copy (or, where required, translation) of statement under Article 19	:	sheets	<input type="checkbox"/>	<input type="checkbox"/>
5. letter	:	sheets	<input type="checkbox"/>	<input type="checkbox"/>
6. other (specify)	:	sheets	<input type="checkbox"/>	<input type="checkbox"/>

The demand is also accompanied by the item(s) marked below:

- | | |
|--|---|
| 1. <input checked="" type="checkbox"/> fee calculation sheet | 4. <input type="checkbox"/> statement explaining lack of signature |
| 2. <input type="checkbox"/> separate signed power of attorney | 5. <input type="checkbox"/> nucleotide and or amino acid sequence listing in computer readable form |
| 3. <input type="checkbox"/> copy of general power of attorney; reference number, if any: | 6. <input type="checkbox"/> other (specify): |

Box No. VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the demand).



ROSS T. MANATON

For International Preliminary Examining Authority use only

- | | | |
|--|---|--|
| 1. Date of actual receipt of DEMAND: | | |
| 2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b): | | |
| 3. <input type="checkbox"/> The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply. | <input type="checkbox"/> The applicant has been informed accordingly. | |
| 4. <input type="checkbox"/> The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5. | | |
| 5. <input type="checkbox"/> Although the date of receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82. | | |

For International Bureau use only

Demand received from IPEA on:

EXTRACTION OF METAL SALTS FROM AQUEOUS SOLUTIONSField of the invention

5 This invention relates to the extraction of metal salts from aqueous solutions. More specifically it relates to methods for extracting metal cations and their associated anions which avoid returning any ionic species to the solution, thus leaving the acidity of the solution unchanged and purifying it by de-ionisation. Methods according to the invention are of use particularly (though not 10 exclusively) in waste remediation and in the recovery of metals from primary sources.

Background

15 Two main methods are currently used for the extraction of metallic ions from solution. Both involve the use of an extractant reagent: in the first method this is mixed with the solution from which the metal ions are to be removed ("solvent extraction"), and in the second it is immobilised on a solid support.

20 Current solvent extraction technology is based on the reaction scheme shown schematically in Figure 1. In this system an acidic extractant is used to remove a metal cation from an aqueous feed stream. The metal n^+ cation is replaced by n protons and the anion is left in the solution. The overall effect on 25 the feed stream is to replace a metal salt MX with a mineral acid H_nX and this leads to an increase in the acidity of the aqueous feed stream.

30 This type of reaction is widely used for the extraction of copper from oxidic ores, the acid introduced into the stream reacting with insoluble metal oxides to give soluble metal salts. Indeed, this reaction scheme is particularly suited to the extraction of metals from metal oxides since the overall reaction has a perfect mass balance equation:



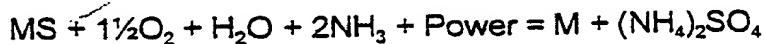
phenolic protons are then displaced and protonate the nitrogen atoms of the tertiary amine groups, producing a positively charged binding site for the anion. The precise binding mechanism for the Type I ligands has yet to be elucidated.

5 Use of either class of ligand is effective to remove both the cations and anions of a metal salt from the feed stream. When decontamination of the feed stream is the sole aim, removal of the metal salt may be regarded as an end in itself. In most cases however, it is desired to extract the cations as elemental metal, and indeed this is the primary aim of ore extraction methods. A major
10 advantage of the method of the invention is that the anion may also be retrieved; for instance the anion (such as sulphate) may be precipitated as an ammonium salt, which may then be used as fertiliser. As a result, this ligand is regenerated in unbound form, and may be recycled for future use.

15 The method of cation and anion precipitation depends on the class of ligand. For Type I ligands, contact with an aqueous ammoniacal solution liberates an ammoniacal solution of the metal salt from which the metal can be electrolysed. The electrolysis step produces metal and acid. Continual addition of ammonia to the system is required to neutralise the acid produced, and a by
20 product of the reaction is an ammonium salt. For Type II ligands, the metal cation M^{**} in the hydrocarbon solution is replaced by n protons generating the 'acid' form of the reagent LH_nX. This allows electrolysis of the metal from an acidic medium. The resulting solution is then contacted with ammonia solution, regenerating the reagent L and producing an ammonium salt as a by product.
25

In each case the overall reaction is the same, and may be represented by the reaction scheme illustrated in Figure 2. The overall mass balance for this system is:

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In a waste remediation application, for example removal of metal salts

from acid mine drainage streams, the reaction scheme is illustrated in Figure 3; the overall mass balance is:



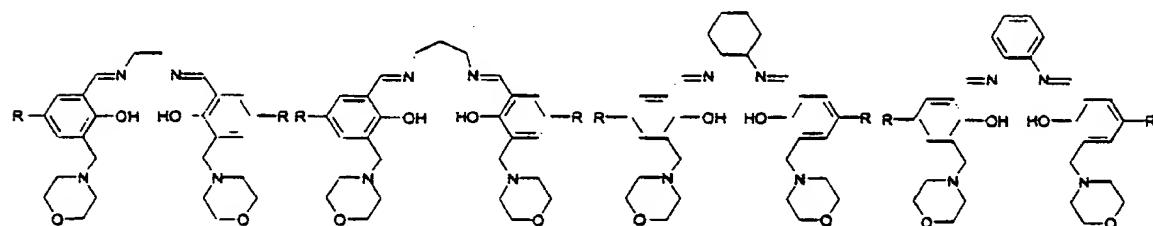
5

The Type I ligands are known in the literature, though not for the purpose of removing metal salts from aqueous solutions as in the present invention; their synthesis will therefore not be described herein. To illustrate the efficacy of ligands of this type in removing metal salts from aqueous solution, a 0.1M 10 solution in toluene of Type I ligand ($R_1 = R_2 = R_3 = -\text{CH}_2\text{CH}_2-$; $R_4=R_5 = \text{C}_9\text{H}_{19}$) was contacted with a 0.1M aqueous solution of nickel sulfate. A light blue toluene solution was formed, analysis of which showed that approximately 80% of both Ni^{2+} and SO_4^{2-} ions had been transferred to the organic phase.

15 Detailed description

The invention is described hereinafter in more detail with reference to the synthesis and activity of various ligands of the Type II formula. The following is a representative sample of various different Type II ligands:

20



25

Me	4	5	6	7
TBu	8	9	10	11
Nonyl	12	13	14	15

CLAIMS

1. A method of extracting both the cation(s) and anion(s) of a metal salt from an aqueous medium, the method comprising the steps of: contacting
5 the aqueous medium with a bifunctional ligand capable of binding both said cation(s) and said anion(s) so as to form a complex comprising said ligand and said cation(s) and anion(s); selectively stripping and recovering said cation(s) and said anion(s) from said complex; and recovering said ligand, free of said cation(s) and anion(s), for future use.

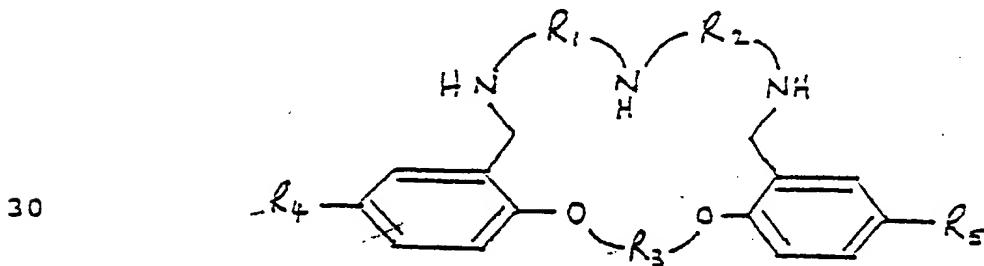
10

2. A method according to claim 1, wherein the ligand has a greater affinity for a water-immiscible extraction medium than it does for said aqueous medium, the method involving the steps of: adding a said water-immiscible extraction medium to said aqueous medium, whereby said ligand with said cation(s) and said anion(s) bound thereto is partitioned preferentially in a water-immiscible phase; and separating said water-immiscible phase with said ligand-bound cation(s) and anion(s) therein from said aqueous medium.

20 3. A method according to claim 1, wherein the ligand is immobilised on or within a solid support.

4. A method according to any of claims 1 to 3, wherein the ligand is of the following formula:

25



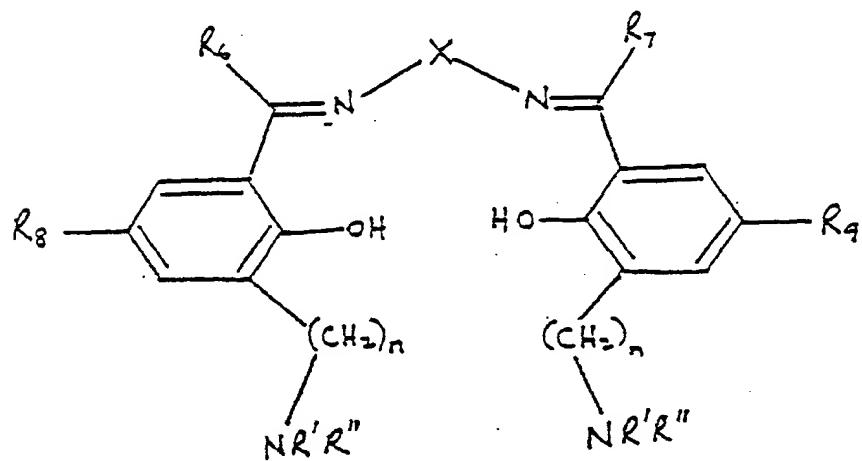
where R_1 , R_2 and R_3 are, independently, substituted C_2 to C_4 linkages; and

5 R_4 and R_5 are, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon group.

10 5. A method according to claim 4, comprising the further steps of: contacting the ligand-bound salt with an aqueous ammoniacal solution to produce an aqueous ammoniacal solution of the metal salt; and electrolysing said solution to produce elemental metal and an ammonium salt.

15 6. A method according to any of claims 1 to 3, wherein the ligand has a cation binding site comprising at least one coordinating acid group and an anion binding site comprising at least one protonatable base.

7. A method according to claim 6, wherein the ligand has the following formula:



25

where: X represents a C₂ to C₄ linkage, in which the carbon atoms may be substituted or unsubstituted and may optionally form part of a ring structure;

5 n = 2, 3 or 4;

R₆, R₇, R₈ and R₉ are each, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon; and

10 R'R" are tertiary amine groups, the R' and R" groups optionally forming a heterocyclic ring.

8. A method according to claim 6 or claim 7, comprising the further
15 steps of: contacting the ligand-bound salt with a strong acid to protonate the ligand and release the metal cation(s); and electrolysing the resulting solution to product elemental metal.

9. A method according to claim 8, comprising the further step of
20 contacting the ligand-bound anion(s) with an ammoniacal solution, to neutralise said solution and produce an ammonium salt.

10. A method according to any of claims 7 to 9, wherein NR'R" is a morpholine or piperidine ring.

25

JY & GW JOHNSON

Chartered Patent Agents
European Patent Attorneys

Regis... Trade Mark Agents
European Trade Mark Attorneys

TELECOPIER

The International Preliminary
Examining Authority
European Patent Office,
D-80298 München,
GERMANY

JC12 Rec'd PCT/PTO 28 SEP 2001

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John R Newby MS(USA) BSc AKC CPA EPA

Kendall R Mann - Accounts

Our Ref

Your Ref

RTM, hmg

21st May 2001

Dear Sirs

International Patent Application PCT/GB00/01251
in the name of The University Court of
The University of Edinburgh

This is in response to the Written Opinion dated 21st December 2000.

I file herewith new pages of the description and claims to replace pages 1, 7, 8, 23, 24 and 25 as currently on file. Pages 1, 7, and 8 have been amended to take into account the Examiner's first point concerning section VII of the Written Opinion. The amendment to the claims has the effect of removing from claim 1 the requirement for recovery of the ions and ligand, since these steps are not essential to the functioning of the invention. Support for this amendment may be found, for instance, at the paragraph commencing at line 24 on page 2 of the original specification, which makes it clear that the essence of the invention is to "extract metal cations from a solution and to simultaneously extract their associated anions". The final sentence of that paragraph reads "Additionally, the ligands we have developed permit both the anions and the cations to be recovered by stripping methods, with the result that the ligand may be then reused". It is also stated (at lines 6 to 9 on page 7) that "When decontamination of the feed stream is the sole aim, removal of the metal salt may be regarded as an end in itself. In most cases, however, it is desired to extract the cations as elemental metal...". It is clear from these passages that the recovery step, although advantageous, is not essential.

The Examiner alleged that original claims 1, 2, 3 and 6 were rendered lacking in novelty with respect to DE 36 07 982 ("D1"). However, I submit that this is not the case and furthermore that D1 does not render amended claim 1 (or any of the other claims) lacking in novelty or in inventive step. In contrast with the bifunctional ligands of the present invention, D1 relates to the

JY & GW JOHNSON

Page 2

21st May 2001

International Patent Application PCT/GB00/01251
in the name of The University Court of
The University of Edinburgh

desalination of water by treatment with an organic solution of an onium salt. The non-aqueous solution of the onium salt is contacted with an aqueous solution containing the ions to be removed, and the cations in the aqueous phase are extracted by the anions of the onium salt into the organic phase. The cations of the onium salt and the anions in the aqueous phase are precipitated. Therefore three phases result. This is an application of a well-known procedure known as metathesis.

In contrast, the method of the present invention involves the use of a bifunctional ligand which extracts both the cation and anion from the aqueous medium, resulting in a neutral complex from which recovery of cation, anion and ligand is readily possible (although not essential, as pointed out above). The claimed method is thus wholly different from that described in D1, and there is no basis for alleging that D1 either anticipates or renders obvious the methods claimed.

As the remaining claims are all dependent from claim 1, I do not believe that it is strictly necessary for me to address the Examiner's further objection to claim 3 (now claim 4). Nevertheless, I believe that it is pertinent to point out that the immobilised ligand of claim 4 is not of the same nature as the solid ion-exchange materials mentioned in the introductory portion of the specification (for example in the paragraph commencing at line 17 on page 2). Ion exchange materials operate by replacing one ion with another, whereas the immobilised ligands of the present invention extract both cations and anions without introducing replacement ions.

I believe that the amendment to the claims will meet the Examiner's objection concerning Section VIII of the Written Opinion, at least insofar as claim 1 is concerned. The language in question now appears in claim 2, but I see no reason why its terms should be in any way unclear to the skilled person. The stripping methods defined in more detail in claims 6, 9 and 10 (previously claims 5, 8 and 9) are merely exemplary and it is not thought appropriate to combine the subject matter of any of these with that of claim 2.

I look forward to receiving a positive International Preliminary Examination Report in due course.

Yours faithfully,


ROSS T. MANATON

EXTRACTION OF METAL SALTS

Field of the invention

5 This invention relates to the extraction of metal salts from aqueous solutions. More specifically it relates to methods for extracting metal cations and their associated anions which avoid returning any ionic species to the solution, thus leaving the acidity of the solution unchanged and purifying it by deionisation. Methods according to the invention are of use particularly (though not 10 exclusively) in waste remediation and in the recovery of metals from primary sources.

Background

15 Two main methods are currently used for the extraction of metallic ions from solution. Both involve the use of an extractant reagent: in the first method this is mixed with the solution from which the metal ions are to be removed ("solvent extraction"), and in the second it is immobilised on a solid support.

20 Current solvent extraction technology is based on a system in which an acidic extractant is used to remove a metal cation from an aqueous feed stream. The metal n^+ cation is replaced by n protons and the anion is left in the solution. The overall effect on the feed stream is to replace a metal salt MX with a mineral acid H_nX and this leads to an increase in the acidity of the aqueous feed stream.

25 This type of reaction is widely used for the extraction of copper from oxidic ores, the acid introduced into the stream reacting with insoluble metal oxides to give soluble metal salts. Indeed, this reaction scheme is particularly suited to the extraction of metals from metal oxides since the overall reaction has a perfect 30 mass balance equation:

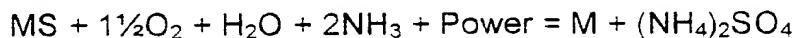


phenolic protons are then displaced and protonate the nitrogen atoms of the tertiary amine groups, producing a positively charged binding site for the anion. The precise binding mechanism for the Type I ligands has yet to be elucidated.

5 Use of either class of ligand is effective to remove both the cations and anions of a metal salt from the feed stream. When decontamination of the feed stream is the sole aim, removal of the metal salt may be regarded as an end in itself. In most cases, however, it is desired to extract the cations as elemental metal, and indeed this is the primary aim of ore extraction methods. A major
10 advantage of the method of the invention is that the anion may also be retrieved; for instance the anion (such as sulphate) may be precipitated as an ammonium salt, which may then be used as fertiliser. As a result, this ligand is regenerated in unbound form, and may be recycled for future use.

15 The method of cation and anion precipitation depends on the class of ligand. For Type I ligands, contact with an aqueous ammoniacal solution liberates an ammoniacal solution of the metal salt from which the metal can be electrolysed. The electrolysis step produces metal and acid. Continual addition of ammonia to the system is required to neutralise the acid produced, and a by
20 product of the reaction is an ammonium salt. For Type II ligands, the metal cation may also be recovered by contacting with strong acid. The metal cation M^{n+} in the hydrocarbon solution is replaced by n protons generating the 'acid' form of the reagent LH_nX . This allows electrolysis of the metal from an acidic medium. The resulting solution is then contacted with ammonia solution, regenerating the reagent L and producing an ammonium salt as a by product.
25

In each case the overall reaction is the same. The overall mass balance for this system is:



30

In a waste remediation application, for example removal of metal salts

from acid drainage streams, the overall mass balance is:



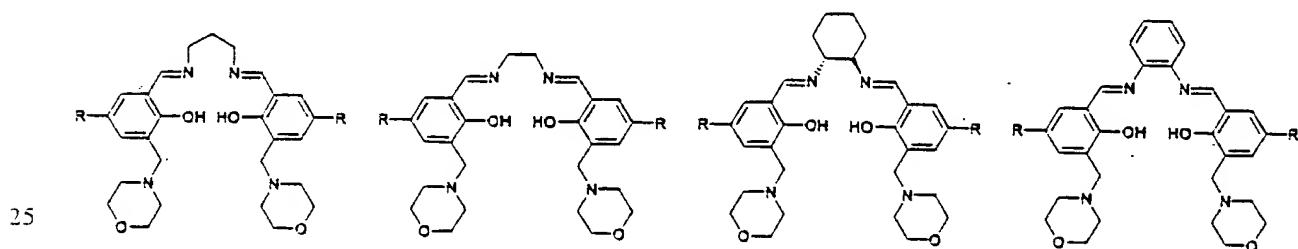
- 5 The Type 1 ligands are known in the literature, though not for the purpose of removing metal salts from aqueous solutions as in the present invention; their synthesis will therefore not be described herein. To illustrate the efficacy of ligands of this type in removing metal salts from aqueous solution, a 0.1M
 10 solution in toluene of Type I ligand ($R_1 = R_2 = R_3 = -\text{CH}_2\text{CH}_2-$; $R_4=R_5=\text{C}_9\text{H}_{19}$) was contacted with an 0.1M aqueous solution of nickel sulfate. A light blue toluene solution was formed, analysis of which showed that approximately 80% of both
 15 Ni^{2+} and SO_4^{2-} -ions had been transferred to the organic phase.

Detailed description

15

The invention is described hereinafter in more detail with reference to the synthesis and activity of various ligands of the Type II formula. The following is a representative sample of various different Type II ligands:

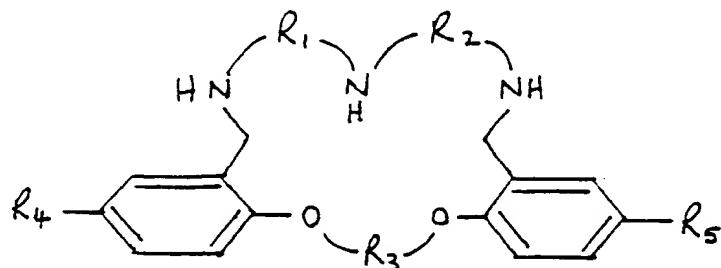
20



Me	4	5	6	7
TBu	8	9	10	11
Nonyl	12	13	14	15

CLAIMS

1. A method of extracting both the cation(s) and anion(s) of a metal salt from an aqueous medium, the method comprising the step of contacting the aqueous medium with a bifunctional ligand capable of binding both said cation(s) and said anion(s) so as to form a complex comprising said ligand and said cation(s) and anion(s).
- 10 2. A method according to claim 1, further comprising the steps of: selectively stripping and recovering said cations(s) and said anions(s) from said complex; and recovering said ligand, free of said cations(s) and anion(s), for future use.
- 15 3. A method according to claim 1 or claim 2, wherein the ligand has a greater affinity for a water-immiscible extraction medium than it does for said aqueous medium, the method involving the steps of: adding a said water-immiscible extraction medium to said aqueous medium, whereby said ligand with said cation(s) and said anion(s) bound thereto is partitioned preferentially in a water-immiscible phase; and separating said water-immiscible phase with said ligand-bound cation(s) and anion(s) therein from said aqueous medium.
- 20 4. A method according to claim 1 or claim 2, wherein the ligand is immobilised on or within a solid support.
- 25 5. A method according to any preceding claim, wherein the ligand is of the following formula:



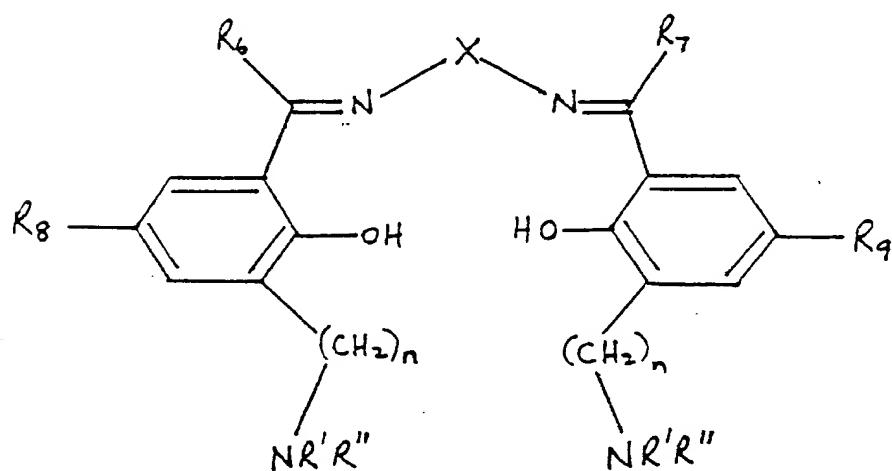
where R_1 , R_2 and R_3 are, independently, substituted C_2 to C_4 linkages; and

R_4 and R_5 are, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon group.

6. A method according to claim 5, comprising the further steps of:
 contacting the ligand-bound salt with an aqueous ammoniacal solution to
 produce an aqueous ammoniacal solution of the metal salt; and electrolysing
 said solution to produce elemental metal and an ammonium salt.

7. A method according to any of claims 1 to 4, wherein the ligand has
 a cation binding site comprising at least one coordinating acid group and an
 anion binding site comprising at least one protonatable base.

8. A method according to claim 5, wherein the ligand has the following formula:



5 where X represents a C_2 to C_4 linkage, in which the carbon atoms may be substituted or unsubstituted and may optionally form part of a ring structure;

n = 2, 3 or 4;

10 R_6 , R_7 , R_8 and R_9 are each, independently, H or an optionally halogenated aliphatic or aromatic hydrocarbon; and

$R'R''$ are tertiary amine groups, the R' and R'' groups optionally forming a heterocyclic ring.

15 9. A method according to claim 7 or claim 8, comprising the further steps of: contacting the ligand-bound salt with a strong acid to protonate the ligand and release the metal cation(s); and electrolysing the resulting solution to product elemental metal.

20 10. A method according to claim 9, comprising the further step of contacting the ligand-bound anion(s) with an ammoniacal solution, to neutralise said solution and produce an ammonium salt.

25 11. A method according to any of claims 8 to 10, wherein $NR'R''$ is a morpholine or piperidine ring.

PCT

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International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C02F 1/68, 1/26	A1	(11) International Publication Number: WO 00/58225 (43) International Publication Date: 5 October 2000 (05.10.00)
(21) International Application Number: PCT/GB00/01251 (22) International Filing Date: 31 March 2000 (31.03.00)		(81) Designated States: JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(30) Priority Data: 9907485.8 31 March 1999 (31.03.99) GB		Published <i>With international search report.</i>
(71) Applicant (<i>for all designated States except US</i>): THE UNIVERSITY COURT OF THE UNIVERSITY OF EDINBURGH [GB/GB]; Old College, South Bridge, Edinburgh EH8 9YL (GB).		
(72) Inventors; and		
(75) Inventors/Applicants (<i>for US only</i>): TASKER, Peter, Anthony [GB/GB]; 25 Braid Avenue, Edinburgh (GB). WHITE, David, James [GB/GB]; 3 Roachill Close, Altrincham, Cheshire (GB).		
(74) Agent: MANATON, Ross, Timothy, J.Y. & G.W. Johnson, Kingsbourne House, 229-231 High Holborn, London WC1V 7DP (GB).		

(54) Title: EXTRACTION OF METAL SALTS FROM AQUEOUS SOLUTIONS

(57) Abstract

A method of removing both the cations and the anions of a metal salt from an aqueous medium, by use of a ligand having binding sites for the cations and anions. The cation binding site comprises at least one coordinating acid group and the anion binding site comprises at least one protonatable base. Using ligands of this type, both the anions and cations may be selectively stripped from the ligand and recovered, and the ligand may thereby be recycled for further use.

INTERNATIO

SEARCH REPORT

Inte Application No

PCT/GB 00/01251

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C02F1/68 C02F1/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 36 07 982 A (LOTTERMOSER MANFRED) 17 September 1987 (1987-09-17) claim 1	1,2

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

4 July 2000

Date of mailing of the international search report

11/07/2000

Name and mailing address of the ISA

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 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Fouquier, J-P

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte Application No

PCT/GB 00/01251

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3607982 A	17-09-1987	NONE	

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

MANATON, R.
J.Y. & G.W. JOHNSON
Kingsbourne House
229-231 High Holborn
London WC1V 7DP
GRANDE BRETAGNE

18 JUN 2001

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing
(day/month/year) 15.06.2001

Applicant's or agent's file reference RTM	IMPORTANT NOTIFICATION	
International application No. PCT/GB00/01251	International filing date (day/month/year) 31/03/2000	Priority date (day/month/year) 31/03/1999
Applicant THE UNIVERSITY COURT OF THE UNIVERSITY OF EDINBURG		

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/ European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Michaleczek, N Tel. +49 89 2399-7254	
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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference RTM	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/GB00/01251	International filing date (day/month/year) 31/03/2000	Priority date (day/month/year) 31/03/1999
International Patent Classification (IPC) or national classification and IPC C02F1/68		
Applicant THE UNIVERSITY COURT OF THE UNIVERSITY OF EDINBURG		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 4 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 6 sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input type="checkbox"/> Certain defects in the international application VIII <input type="checkbox"/> Certain observations on the international application 		

Date of submission of the demand 26/10/2000	Date of completion of this report 15.06.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Grigoraki, E Telephone No. +49 89 2399 8353



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB00/01251

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):
Description, pages:

2-6,9-22 as originally filed

1,7,8 as received on 24/05/2001 with letter of 21/05/2001

Claims, No.:

1-11 as received on 24/05/2001 with letter of 21/05/2001

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:
- the drawings, sheets:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB00/01251

5. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims 2-11
	No:	Claims 1
Inventive step (IS)	Yes:	Claims 2-11
	No:	Claims 1
Industrial applicability (IA)	Yes:	Claims 1-11
	No:	Claims

2. Citations and explanations
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB00/01251

Conc. section V:

(1)

As acknowledged in the description, on page 3, l. 1-20 of the description, bifunctional ligands for simultaneous binding of cations and anions are already known. Present claim 1 now defining in a broader manner than originally a method of extracting both the cations and anions of a metal salt from an aqueous medium by contacting it with such bifunctional ligand is not considered novel or is at least not inventive in view of the cited prior art on page 3 of the application.

Claim 1 does not therefore fulfil the requirements of article 33(2) or (3) PCT.

(2)

The above cited prior art in the application apparently does not suggest the effective multiple use of such ligands after binding cations and anions from aqueous media and selectively stripping and recovering them from the thus obtained complex.

DE-A-3607982 (D1) cited in search report apparently does not disclose the use of bifunctional ligands and the formation of a complex with all three of them. D1 moreover uses onium salts the cations of which form with anions of the aqueous phase non soluble salts in the organic phase and the anions thereof form with the cations of the aqueous phase soluble salts which are precipitated.

The use of such bifunctional ligands with the purpose of recovering the cations and anions from an aqueous medium and upon stripping recovering the ligand for reuse as defined in present claim 2 can be regarded as a novel and inventive concept.

Claim 2 in combination with claim 1 and dependent claims thereon 3-11 would therefore fulfil the requirements of article 33(2) and (3) PCT.

PCT REQUEST

RTM3

Original (for SUBMISSION) - printed on 31.03.2000 06:21:33 PM

0 0-1	For receiving Office use only International Application No.	
0-2	International Filing Date	
0-3	Name of receiving Office and "PCT International Application"	
0-4 0-4-1	Form - PCT/RO/101 PCT Request Prepared using	PCT-EASY Version 2.90 (updated 08.03.2000)
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.	
0-6	Receiving Office (specified by the applicant)	United Kingdom Patent Office (RO/GB)
0-7	Applicant's or agent's file reference	RTM3
I	Title of invention	EXTRACTION OF METAL SALTS
II	Applicant This person is:	applicant only
II-1	Applicant for	all designated States except US
II-4	Name	THE UNIVERSITY COURT OF THE UNIVERSITY OF EDINBURGH
II-5	Address:	Old College South Bridge Edinburgh, EH8 9YL
II-6	State of nationality	United Kingdom
II-7	State of residence	GB
III-1	Applicant and/or inventor This person is:	applicant and inventor
III-1-1	Applicant for	US only
III-1-4	Name (LAST, First)	TASKER, Peter A
III-1-5	Address:	25 Braid Avenue Edinburgh, United Kingdom
III-1-6	State of nationality	GB
III-1-7	State of residence	GB

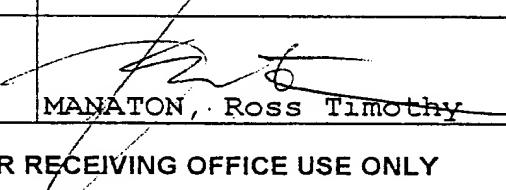
PCT REQUEST

Original (for SUBMISSION) - printed on 31.03.2000 06:21:33 PM

III-2	Applicant and/or inventor	
III-2-1	This person is:	
III-2-2	Applicant for	
III-2-4	Name (LAST, First)	
III-2-5	Address:	
III-2-6	State of nationality	
III-2-7	State of residence	
IV-1	Agent or common representative; or address for correspondence	
The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:		
IV-1-1	Name (LAST, First)	
IV-1-2	Address:	
IV-1-3	Telephone No.	
IV-1-4	Facsimile No.	
V	Designation of States	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	
V-5	Precautionary Designation Statement In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.	
V-6	Exclusion(s) from precautionary designations	
	NONE	

PCT REQUEST

Original (for SUBMISSION) - printed on 31.03.2000 06:21:33 PM

VI-1	Priority claim of earlier national application		
VI-1-1	Filing date	31 March 1999 (31.03.1999)	
VI-1-2	Number	9907485.8	
VI-1-3	Country	GB	
VII-1	International Searching Authority Chosen	European Patent Office (EPO) (ISA/EP)	
VIII	Check list	number of sheets	electronic file(s) attached
VIII-1	Request	3	-
VIII-2	Description	22	-
VIII-3	Claims	3	-
VIII-4	Abstract	1	abstract.txt
VIII-5	Drawings	0	-
VIII-7	TOTAL	29	
VIII-8	Accompanying items	paper document(s) attached	electronic file(s) attached
VIII-12	Fee calculation sheet	✓	-
VIII-16	Priority document(s)	Item(s) VI-1	-
VIII-18	PCT-EASY diskette	-	diskette
VIII-19	Figure of the drawings which should accompany the abstract		
IX-1	Language of filing of the international application	English	
IX-1-1	Name (LAST, First)	 MANATON, Ross Timothy	

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10-1	Date of actual receipt of the purported international application	
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/EP
10-6	Transmittal of search copy delayed until search fee is paid	

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11-1	Date of receipt of the record copy by the International Bureau	
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PATENT COOPERATION TREATY

From the:
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

MANATON, R.
J.Y. & G.W. JOHNSON
Kingsbourne House
229-231 High Holborn
London WC1V 7DP
GRANDE BRETAGNE 27 DEC 2000

SEARCHED

PCT

WRITTEN OPINION

(PCT Rule 66)

		Date of mailing (day/month/year) 21.12.2000
Applicant's or agent's file reference RTM		REPLY DUE within 3 month(s) from the above date of mailing
International application No. PCT/GB00/01251	International filing date (day/month/year) 31/03/2000	Priority date (day/month/year) 31/03/1999
International Patent Classification (IPC) or both national classification and IPC C02F1/68		
Applicant THE UNIVERSITY COURT OF THE UNIVERSITY OF EDINBURG		

1. This written opinion is the first drawn up by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

- I Basis of the opinion
- II Priority
- III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV Lack of unity of invention
- V Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI Certain document cited
- VII Certain defects in the international application
- VIII Certain observations on the international application

3. The applicant is hereby invited to reply to this opinion.

When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also: For an additional opportunity to submit amendments, see Rule 66.4. For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 bis. For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 31/07/2001.

Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer / Examiner Grigoraki, E Formalities officer (incl. extension of time limits) Gregoire, J-P Telephone No. +49 89 2399 8041
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WRITTEN OPINION

International application No. PCT/GB00/01251

I. Basis of the opinion

1. This opinion has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed".*):

Description, pages:

1-22 as originally filed

Claims, No.:

1-10 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:
- the drawings, sheets:

WRITTEN OPINIONInternational application No. PCT/GB00/01251

5. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**1. Statement**

Novelty (N) Claims 1,2,6

Inventive step (IS) Claims 3

Industrial applicability (IA) Claims

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Conc. Section V:

Reference is made to the following document:

D1: DE 36 07 982 A

claims 1,2,3,6:

D1 discloses a method of extracting both the cation(s) and anions(s) of a metal salt from an aqueous medium by contacting said medium with a bifunctional ligand. D1 appears to be novelty destroying for the subject matter of claims 1, 2 and 6.

Claims 1, 2 and 6 do not fulfil the requirements of article 33(2) PCT.

The subject matter of claim 3 is apparently known in the art as acknowledged also in the description so that said claim does not define an inventive concept; claim 3 does not fulfil the requirements of article 33(3) PCT.

claims 4,5,7-10:

The method using the ligands as defined in claims 4 and 6 is novel and is also considered inventive in view of D1. Claims 4,5 and 7-10 fulfil therefore the requirements of articles 33(2) and (3) PCT.

Conc. Section VIII:

The step of recovering the cations/anions and ligand is not clearly defined so that claim 1 is objectionable under article 6 PCT. To overcome this objection the subject matter of claims 5 or 8/9 appears to be essential to be incorporated into claim 1.

Conc. Section VII:

> The reference to figures 1,2 and 3 on pages 1 and 7/8 of the description is not understandable since no such figures were found in the original documents; any such reference in the description should therefore be deleted.

>> To be in accordance with the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the document D1 should be mentioned in the description.



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Correspondence with the EPO on PCT Chapter II demands

In order to ensure that your PCT Chapter II demand is dealt with as promptly as possible you are requested to use the enclosed self-adhesive labels with any correspondence relating to the demand sent to the Munich Office.

One of these labels should be affixed to a prominent place in the upper part of the letter or form etc. which you are filing.